Understanding Secondary Organic Aerosol (SOA) Formation from Lower-Volatility Precursors: Photooxidation of Naphthalene and Alkyl-naphthalenes

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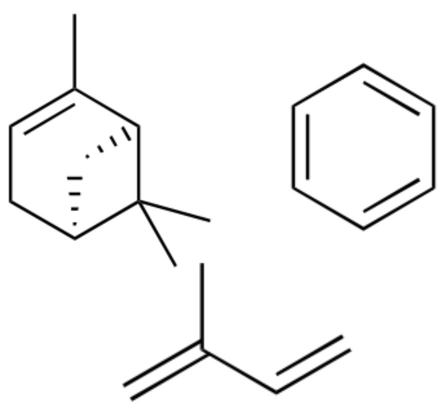
Organic Aerosol

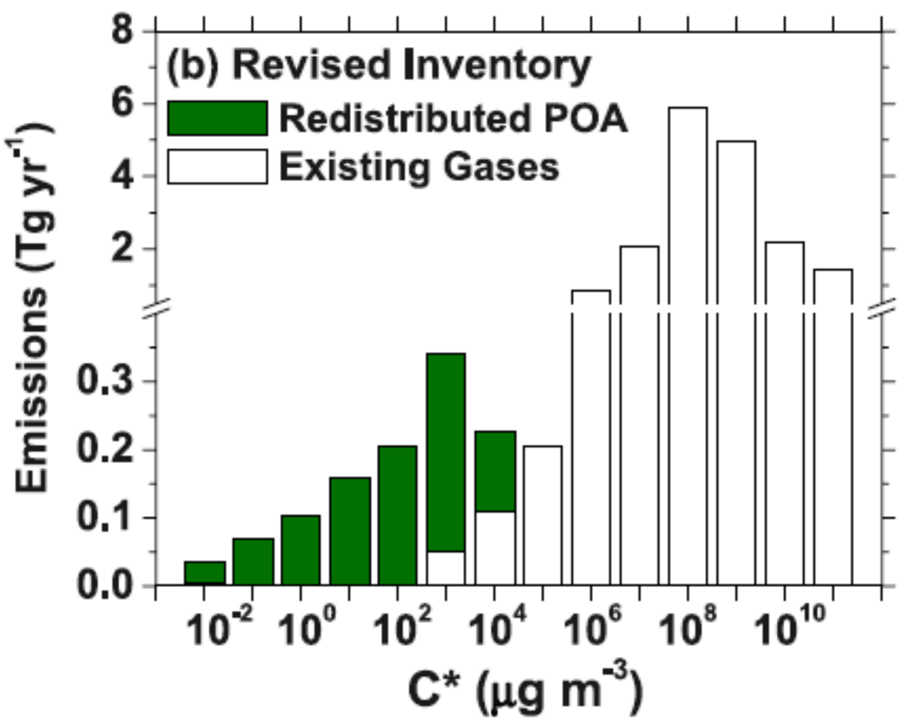
- Primary (POA)- Traditional view
  - directly emitted
  - nonvolatile
  - static

- Secondary (SOA)

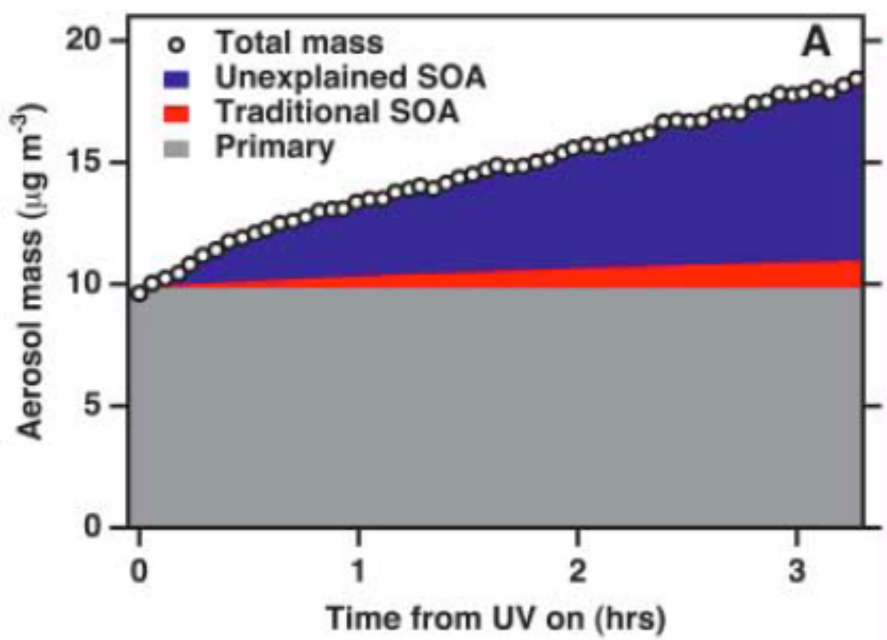


$\xrightarrow{\text{atmospheric oxidation}}$ condensable products

Semivolatile Emissions



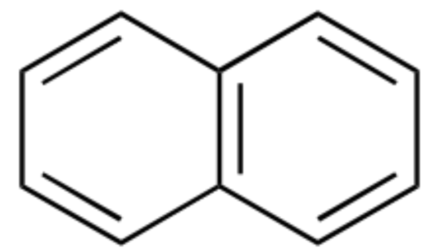
Shrivastava et al., JGR 2008



Robinson et al., Science 2007

Naphthalene

- Most abundant polycyclic aromatic hydrocarbon (PAH)
- Sources:
  - Wood burning
  - Diesel exhaust
  - Gasoline exhaust



- Sink:
  - Reaction with OH (lifetime of 5.5 h)

- Objective: to study SOA formation from PAHs and calculate the contribution of PAH oxidation to SOA formed from semi-volatile emissions

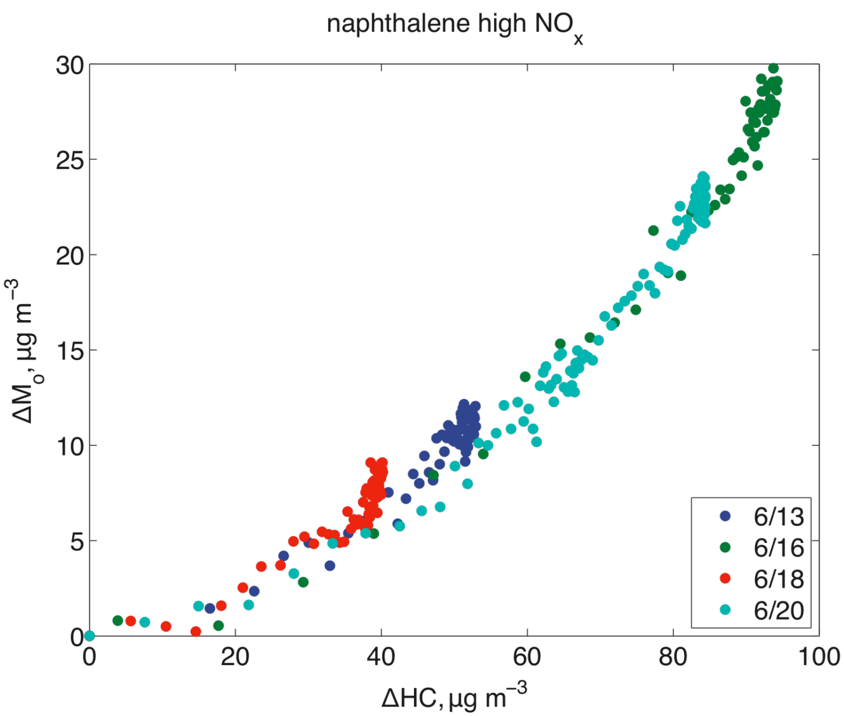
Experimental

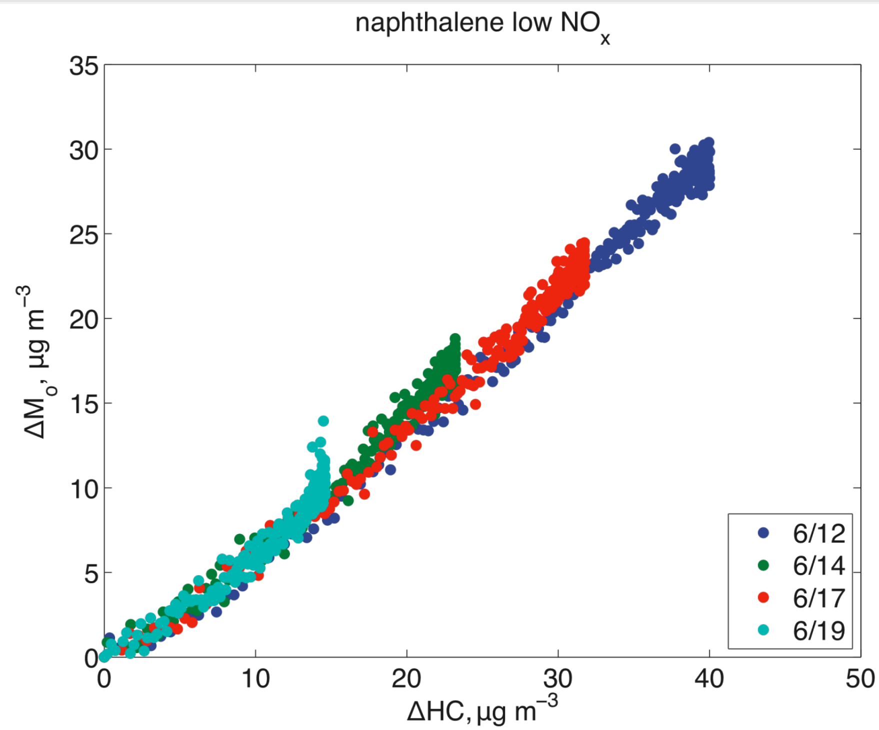
- High- and Low-NO_x:
  - High NO_x: HONO + hv → OH + NO (NO added)
  - Low NO_x: H_2O_2 + hv → OH + OH
- T ≈ 299K, RH < 10%
- Ammonium sulfate seed, volume ≈ 15 μm^3 cm^{-3}
- Also: 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), 1,2-dimethylnaphthalene (1,2-DMN)

Instrumentation

- Dual 28-m^3 chambers
- Gas phase:
  - GC/FID (naphthalene, 1-MN, 2-MN, 1,2-DMN)
  - GC/TOF-MS (gas-phase intermediates)
  - CIMS (+/-) (gas-phase intermediates)
  - O_3, NO/NO_x, NO_2
- Aerosol phase:
  - DMA (aerosol size distribution, volume conc)
  - AMS (aerosol composition, density)
  - Filter sampling -> UPLC/ESI-TOFMS, HPLC/ESI-ITMS (aerosol composition)

Aerosol Yields from PAHs

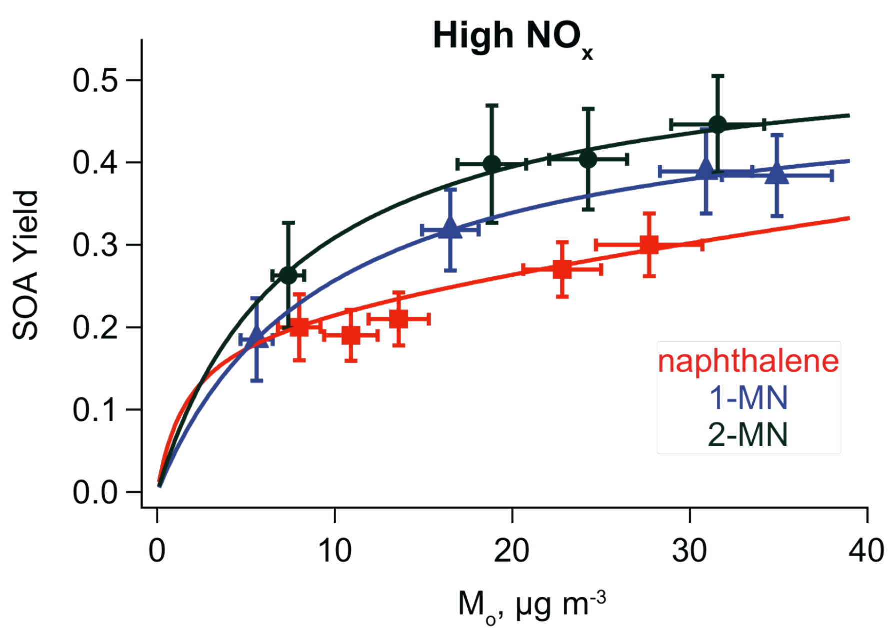




- As with virtually all SOA systems, low-NO_x yields are higher
- Only exception are sesquiterpenes, where nitrates are formed

Aerosol Yields from PAHs

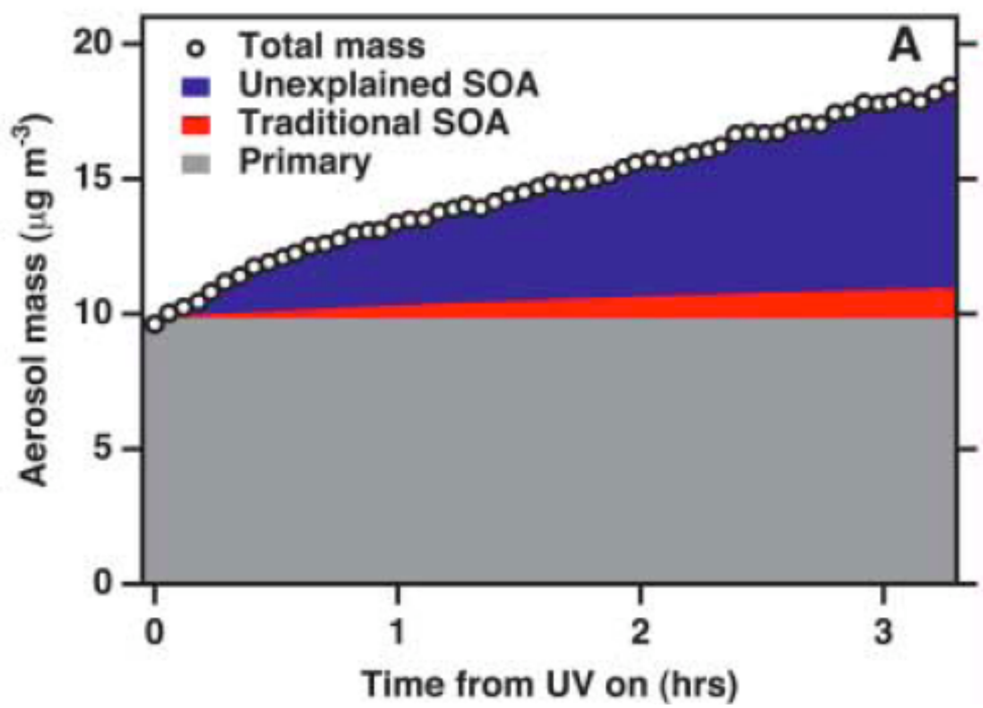
High NO_x Yield Curves



$$Y = \frac{\Delta M_O}{\Delta HC} = M_O \sum_{i=1}^{n} \frac{\alpha_i K_i}{1 + K_i M_O}$$

	α_1	K_1, m^3 μg^{-1}	α_2	K_2, m^3 μg^{-1}	SOA Yield @ 15 μg m^{-3}
high NO_x					
naphthalene	0.21	0.59	1.07	0.0037	0.26
1-MN	0.50	0.11	--	--	0.33
2-MN	0.55	0.13	--	--	0.38
1,2-DMN	0.31	n/a	--	--	0.31
low NO_x					
naphthalene	0.73	n/a	--	--	0.73
1-MN	0.68	n/a	--	--	0.68
2-MN	0.58	n/a	--	--	0.58

Explaining the "Unexplained"



Robinson et al., Science 2007

- Only 15% of the SOA is from "traditional" precursors:
  - 90% of this is accounted for by light aromatics (benzene, toluene, xylenes, trimethylbenzenes)
  - Estimated from PTR-MS measurements of these precursors, and yields from SOAM II (Koo et al., Atmos Env., 1997)

- How much SOA do PAHs contribute to the "unexplained" SOA?

Diesel Exhaust

- Emission profile of medium-duty diesel engine (Schauer et al., ES&T, 1999)

Light aromatics

PAHs we studied

Aromatic Hydrocarbons									
benzene	2740		*h*	*a, e*	C_1-fluorene	65.2	83.0	190	*b, f*
toluene	3980		*h*	*a, e*	phenanthrene	93.1	47.0	57	*a, f*
ethylbenzene	470		*h*	*a, e*	anthracene	12.5	10.9	5	*a, f*
m- and *p*-xylene	2330		*h*	*a, e*	3-methylphenanthrene	30.3	29.4	51	*b, f*
o-xylene	830		*h*	*a, e*	2-methylphenathrene	42.0	35.6	45	*b, f*
n-propylbenzene	100		*h*	*a, e*	2-methylanthracene	10.4	10.4	6	*a, f*
p-ethyltoluene	520		*h*	*a, e*	9-methylphenanthrene	22.9	22.0	35	*b, f*
m-ethyltoluene	210		*h*	*a, e*	1-methylphenanthrene	17.0	17.8	28	*a, f*
1,3,5-trimethylbenzene	260		*h*	*a, e*	C_2-MW 178 PAH	196	57.2	2080	*a, f*
1,2,4-trimethylbenzene	880		*h*	*a, e*	C_3-MW 178 PAH	97.4	97.5	120	*b, f*
naphthalene[l]	617		600	*a, f*	fluoranthene	53.0	56.6		*a, f*
2-methylnaphthalene[l]	611		980	*a, f*	acephenanthrylene	12.0	16.2		*b, f*
1-methylnaphthalene[l]	378		580	*a, f*	pyrene	71.9	88.5	64	*a, f*
C_2-naphthalenes	542		2050	*a, f*	C_1-MW 202 PAH	39.0	81.0	290	*b, f*
C_3-naphthalenes	240	130	1360	*b, f*	benzo[*ghi*]fluoranthene	5.82	19.8		*b, f*
C_4-naphthalenes	97.3	98.6	760	*b, f*	cyclopenta[*cd*]pyrene	2.06	3.50		*a, f*
acenaphthylene	70.1			*a, f*	benz[*a*]anthracene	2.98	7.76		*a, f*
acenaphthene	19.3			*a, f*	chrysene and triphenylene	3.35	15.6		*a, f*
fluorene	34.6	9.5	52	*a, f*	C_1-MW 228 PAH		6.54		*b, f*

  - Similar to engine used in Robinson et al. (2007) (same toluene : particle mass ratio)

- k_{OH} for different compounds to estimate the amount of HC reacted at any given time
- SOA Yields from high-NO_x photooxidation of benzene, toluene and *m*-xylene under similar conditions (OH precursor, lights etc.) (Ng et al., ACP, 2007)

Contribution of PAH to SOA

	SOA formed (μg km^{-1})		
	after 3 h	after 12 h	after 24 h
Light aromatics			
benzene	14	53	101
toluene	47	158	255
ethylbenzene	7	22	34
xylene	35	96	126
o-xylene	19	43	49
n-propylbenzene	3	7	9
p-ethyltoluene	12	34	47
m-ethyltoluene	7	17	21
1,3,5-TMB	11	15	16
1,2,4-TMB	27	49	52
Total	**182**	**496**	**710**
PAHs			
naphthalene	62	136	155
2-methylnaphthalene	152	231	234
1-methylnaphthalene	73	120	124
C2-naphthalenes	122	167	168
C3-naphthalenes	61	74	74
C4-naphthalenes	25	30	30
other	226	275	275
Total	**721**	**1033**	**1060**

- Amount of SOA from PAH photooxidation is greater than that from light aromatics
- Why?
  - PAH oxidation products are less volatile (higher SOA yield)
  - PAH oxidation is faster
- Offsets the difference in emissions

Other Semivolatile Emissions

Light aromatics		PAHs		n-alkanes	
benzene	14	naphthalene	62	dodecane	2
toluene	47	2-methylnaphthalene	152	tridecane	4
ethylbenzene	7	1-methylnaphthalene	73	tetradecane	10
xylene	35	C2-naphthalenes	122	pentadecane	11
o-xylene	19	C3-naphthalenes	61	hexadecane	34
n-propylbenzene	3	C4-naphthalenes	25	heptadecane	55
p-ethyltoluene	12	other	226	octadecane	96
m-ethyltoluene	7			nonadecane	105
1,3,5-TMB	11			eicosane	104
1,2,4-TMB	27				
Total for light aromatics	**182**	**Total for PAHs**	**721**	**Total for n-alkanes**	**420**

- After 3 h of photooxidation, PAHs and *n*-alkanes can account for up to 86% of the SOA, or all of the “unexplained” SOA

Other Semivolatile Emissions

- Other sources of POA:

Source	PAH SOA / light aromatic SOA (after 12 h)
Diesel	2.08
Gasoline	0.18
Meat Cooking*	0.25
Vegetable Cooking*	10.22
Wood Combustion	4.44

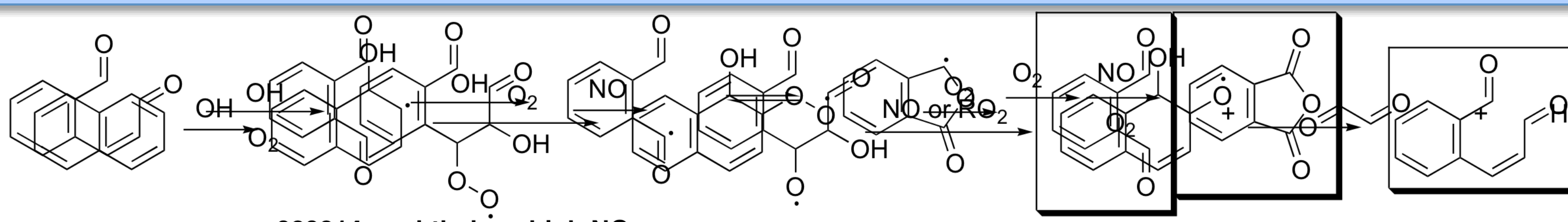
Schauer et al., ES&T, 1999ab, 2001ab, 2002

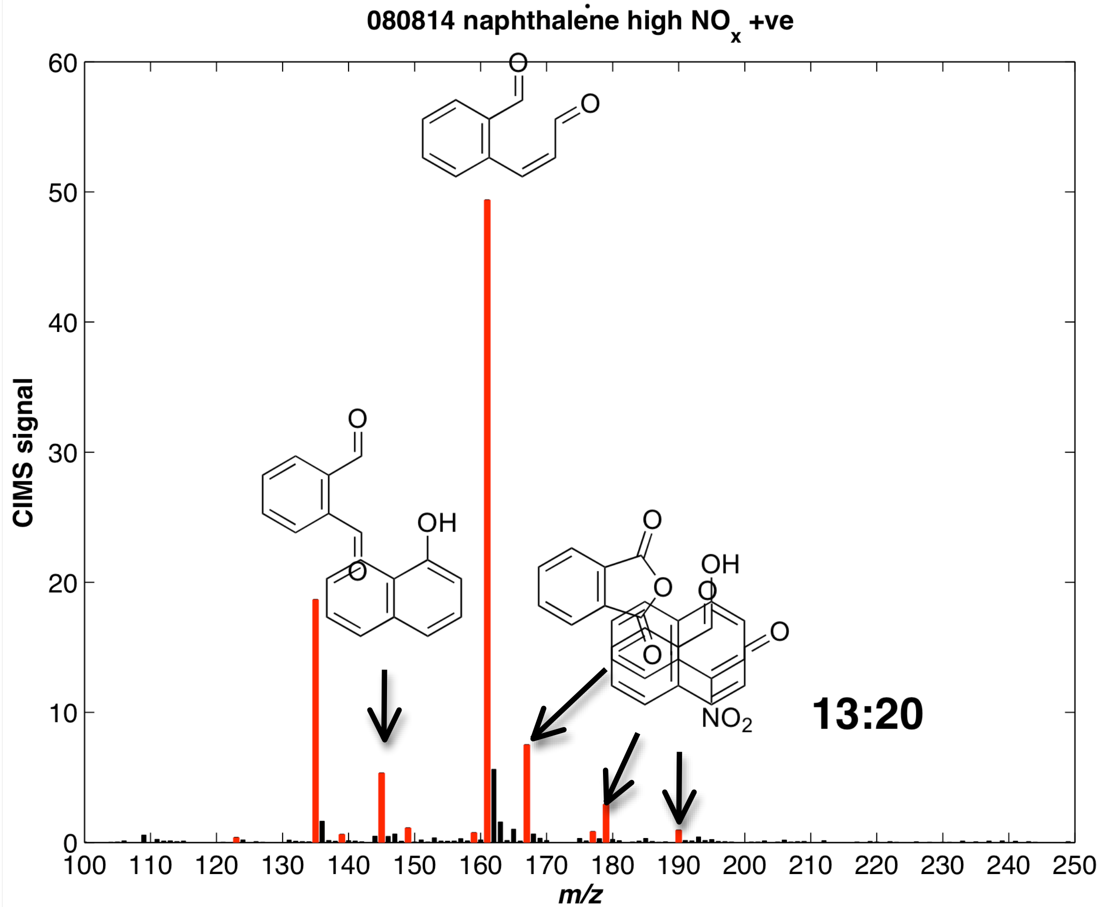
- Emissions from meat and vegetable cooking consist mainly of aliphatic aldehydes, not aromatic hydrocarbons

Conclusions

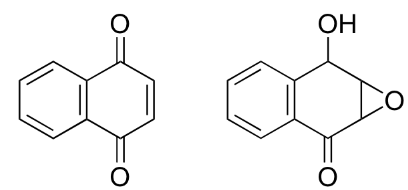
- Photooxidation of naphthalene and alkylnaphthalenes forms SOA with relatively high yields
- Under high NO_x, SOA is semivolatile, likely due to ring-opening pathways; under low NO_x, more ring-retaining products are observed in the gas-phase, and SOA appears nonvolatile
- Together with *n*-alkanes, PAHs likely account for a substantial fraction of SOA formed from further oxidation of semivolatile diesel emissions
- More work is needed to study formation of SOA for other semivolatile compounds (*n*-alkanes, aliphatic aldehydes, large olefins)
- IVOCs explain part of the “missing OA” in the atmosphere

Gas-phase mechanism: Naphthalene high NO_x





- CIMS (+): VOC + n H_2O + H^+ → $[VOC + H]^+ \,.\, n\, H_2O$
- Initial: 47 ppb naphthalene
- Reacted: 15 ppb naphthalene
- Fragmentation dominates due to RO_2 + NO reaction
- Other products:



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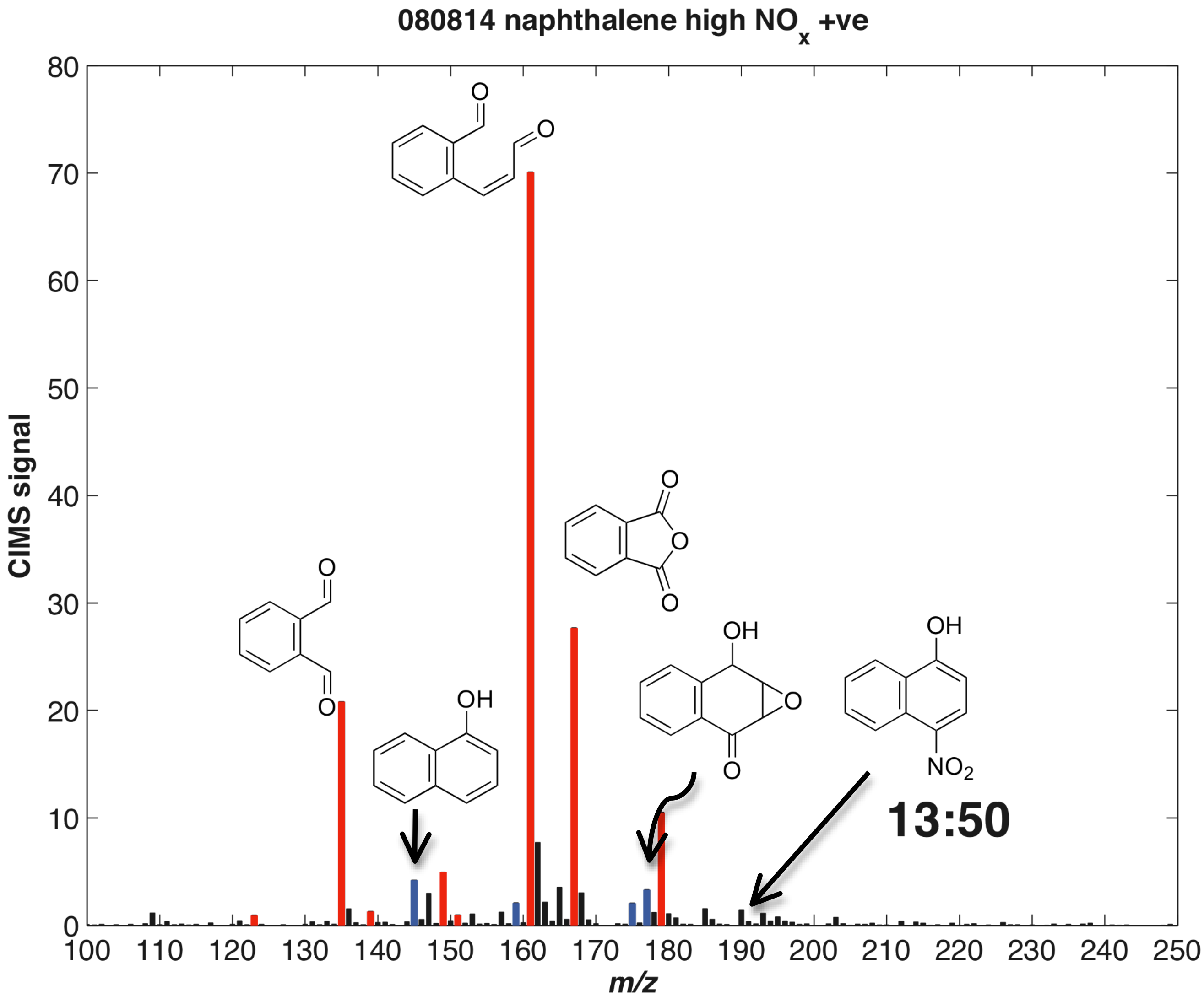
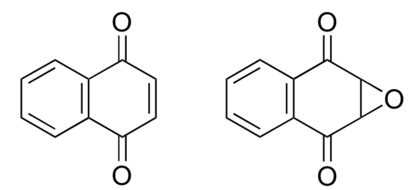
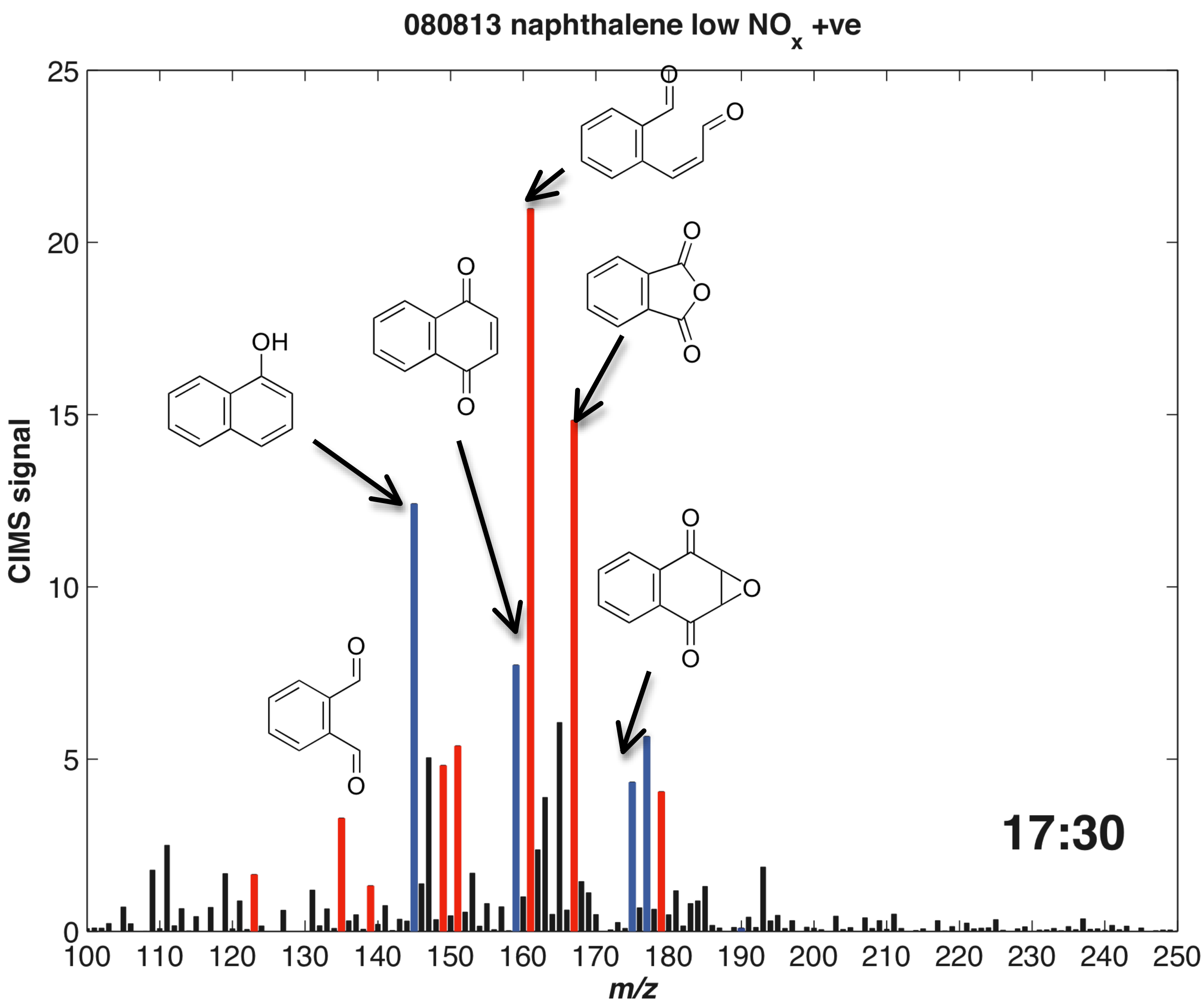


Other products:



- Initial: 47 ppb
- Reacted: 31 ppb

Gas-phase Mechanism: Naphthalene Low NO_x

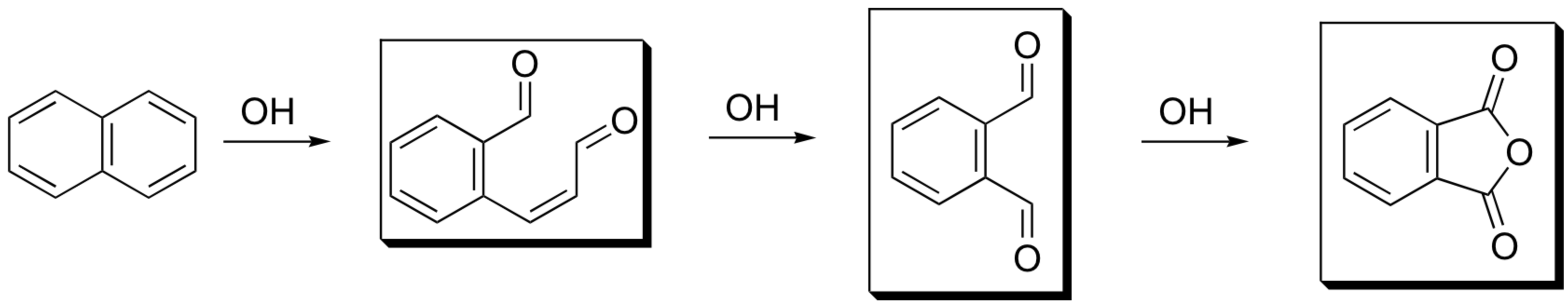


- Initial: 67 ppb
- Reacted: 45 ppb

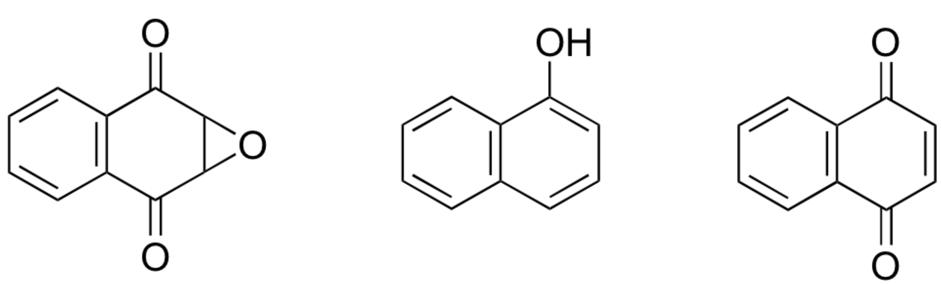
- Relative importance of ring-retaining reactions higher

Gas-phase intermediates

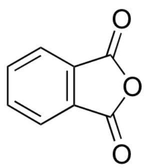
- Ring-opening products (high- and low-NO_x):



- Ring-retaining products (low-NO_x):



Aerosol Composition



Naphthalene + HONO + NO + ammonium sulfate seed